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Form Approved

OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY) 18-Apr-2014				2. REPORT TYPE Final		3. DATES COVERED (From - To) 18 Sep 12 to 17 Sep 13	
4. TITLE AND SUBTITLE  Nucleation and growth control of ZnO via impurity-mediated crystallization				5a. CONTRACT NUMBER FA2386-12-1-4094			
				5b. GRANT NUMBER Grant AOARD-124094			
				5c. PROGRAM ELEMENT NUMBER 61102F			
6. AUTHOR(S)  Prof Hidetoshi Matsumoto				5d. PROJECT NUMBER			
				5e. TASK NUMBER			
				5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Tokyo Institute of Technology 2-12-1-S8-27, Ookayama, Meguro-ku Tokyo 152-8552 Japan				8. PERFORMING ORGANIZATION REPORT NUMBER  N/A			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AOARD UNIT 45002 APO AP 96338-5002				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR/IOA(AOARD)			
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AOARD-124094			
12. DISTRIBUTION/AVAILABILITY STATEMENT  Distribution A: Approved for public release. Distribution is unlimited.							
13. SUPPLEMENTARY NOTES							
14. ABSTRACT The goal of this research project is to develop highly conductive graphene composite carbon nanofiber (CNF) webs with an electrical conductivity larger than $1 \times 10^3$ S/cm. In addition, metal-oxide-nanostructures on the surface of CNF webs will also be developed. These highly conductive and surface-modified CNF webs will be utilized for high-performance electrodes of energy storage devices including flexible ones.							
15. SUBJECT TERMS  Conductors, Composite Materials, Graphene, nano-fibers							
16. SECURITY CLASSIFICATION OF: a. REPORT    b. ABSTRACT    c. THIS PAGE U            U            U			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON Seng Hong, Ph.D.  19b. TELEPHONE NUMBER (Include area code) +81-42-511-2000		

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1. REPORT DATE <b>18 APR 2014</b>	2. REPORT TYPE <b>Final</b>	3. DATES COVERED <b>18-09-2012 to 17-09-2013</b>		
4. TITLE AND SUBTITLE <b>Nucleation and growth control of ZnO via impurity-mediated crystallization</b>			5a. CONTRACT NUMBER <b>FA2386-12-1-4094</b>	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER <b>61102F</b>	
6. AUTHOR(S) <b>Hidetoshi Matsumoto</b>			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Tokyo Institute of Technology, 2-12-1-S8-27, ,Ookayama, Meguro-ku, Tokyo, JP, 152-8552</b>			8. PERFORMING ORGANIZATION REPORT NUMBER <b>N/A</b>	
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16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>5</b>
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>		

# Final Report of “Graphene-Composite Carbon Nanofiber-Based Electrodes for Energy Storage Devices” (Grant No. FA2386-12-1-4094)

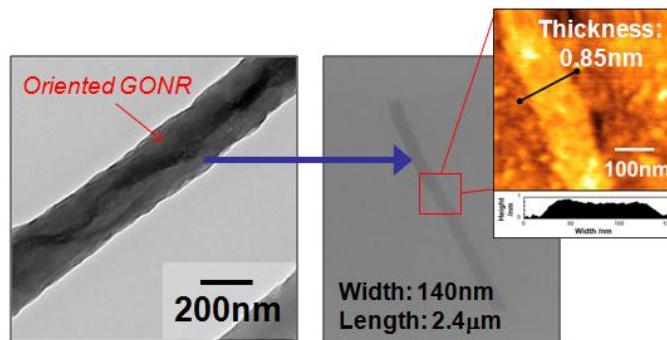
Hidetoshi Matsumoto

Department of Organic and Polymeric Materials, Tokyo Institute of Technology

Carbon nanomaterials, carbon nanotubes (CNTs), carbon nanofibers (CNFs), and graphenes, have attracted a considerable amount of attention in energy conversion and storage fields such as electrodes, conductive additives, and capacitors because of their high surface area, good electrical conductivities, and chemical stability. The goal of this research project is to develop highly conductive graphene composite CNF webs with an electrical conductivity larger than 1000 S/cm. In addition, metal-oxide-nanostructures on the surface of CNF webs were developed. The developed CNF webs were utilized for electrodes of electrochemical supercapacitors.

## 1. Development of highly conductive graphene composite CNF webs

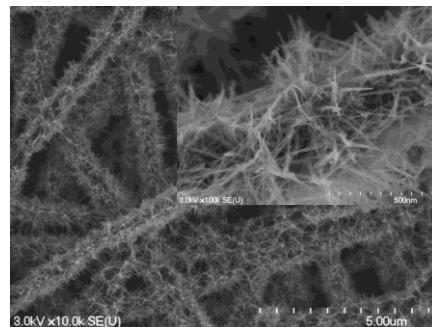
Graphene, a single-atom-thick sheet of  $sp^2$  bonded carbon atoms, have received considerable interest due to their extraordinary electronic properties. Herein we used graphene nanoribbon (GNR), thin elongated stripes of graphene, as a conductive filler of CNFs. The GNR/carbon composite nanofibers were prepared by electrospinning from poly(acrylonitrile) (PAN) containing graphene oxide nanoribbons (GONRs), and successive twisting and carbonization. The electrospinning process can exert directional shear force coupling with the external electric field to the flow of the spinning solution. During electrospinning, the well-dispersed GONRs were highly oriented along the fiber axis in an electrified thin liquid jet (**Figure 1**). The addition of GONRs at a low weight fraction significantly improved the mechanical properties of the composite nanofibers. In addition, the carbonization of the matrix polymer enhanced not only the mechanical but also the electrical properties of the composites (the more detailed data are included in the attached PDF file). The oriented GONRs contained in the PAN nanofibers effectively functioned as not only the one-dimensional nanofiller but also the nanoplatelet promoter of stabilization and template agent for the carbonization and enhanced the electrical conductivity of the GNR/carbon composite nanofiber webs (up to more than 150 S/cm for apparent surface conductivity of the webs) and yarns (up to more than 500 S/cm). At present, the optimization of graphitization process at higher than 1500 °C are now in progress to improve the electrical conductivity



**Figure 1** Scanning electron micrograph of the electrospun PAN composite nanofibers containing oriented graphene oxide nanoribbons prepared by unzipping of multi-walled carbon nanotubes.

## 2. Surface modification of highly conductive CNF webs with metal-oxide nanostructures

We prepared hierarchy-structured CNF webs by electrodeposition of nanostructured manganese oxide ( $\text{MnO}_x$ ) on CNFs. The electrodeposition were conducted in a standard three-electrode cell (CNF webs were used as the substrate of the deposition). The surface of the CNFs was covered with the needle-like  $\text{MnO}_x$  nanowires ( $\text{MnO}_x$  NWs) after the deposition (**Figure 2**). The X-ray diffraction analysis also revealed that the nanowires have a  $\gamma\text{-MnO}_2$  crystalline phase.

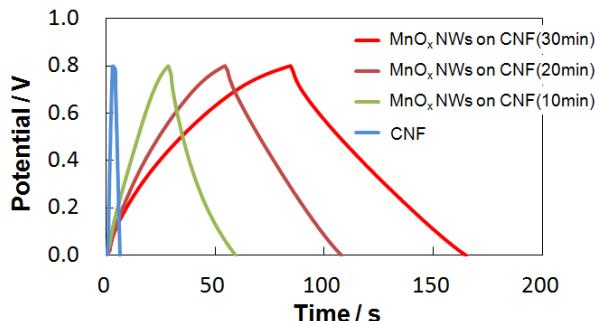


**Figure 2** Typical scanning electron micrograph of CNF webs after electrodeposition. (Inset) a micrograph with large magnification.

## 3. Performance evaluation of energy storage devices with CNF web electrodes

To estimate the potentiality of the developed CNF webs, we fabricated CNF/ $\text{MnO}_2$ -based electrochemical supercapacitors and evaluated their performance. The capacitance increased with an increase in the amount of  $\text{MnO}_2$  NWs (duration of the deposition) (**Figure 3**). This indicates that the hierarchy-structured CNF electrode facilitates the electrochemical reaction at the surface of  $\text{MnO}_2$  NWs due to their large

surface area and the charge transportation by their CNF network structure.



**Figure 3** Charge/discharge curves of CNF webs after electrodeposition with various duration.

### Researchers

Name	Organization, Division	Title	Degree	Specialty
Hidetoshi Matsumoto	Tokyo Institute of Technology, Graduate School of Science and Engineering	Associate Professor	Dr. Eng.	Nanomaterials Energy Conversion
Akihiko Tanioka	Tokyo Institute of Technology, Graduate School of Science and Engineering	Professor Emirates	Dr. Eng.	Polymer Structure & Property
Mamoru Meguro	Tokyo Institute of Technology, Graduate School of Science and Engineering	Graduate student	B.Eng.	Nanofibers Electrochemistry

### Publications

1. “Electrospun composite nanofiber yarns containing oriented graphene nanoribbons” H. Matsumoto\*, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka, W. Lu, J. M. Tour  
*ACS Applied Materials & Interfaces*, **5(13)**, 6225-6231, July 2013. (Please see attached PDF file)

### Presentations

#### International

1. “Enhancement of electrical and mechanical properties of electrospun composite nanofiber yarns containing oriented graphene nanoribbons” H. Matsumoto, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka, W. Lu, J. M. Tour

Electrospinning and Nanofibers: Symposium in Honor of the 85th Birthday of Darrell Reneker, Meeting: 247th ACS National Meeting, Dallas, TX, USA March 16-20, 2014. *Abstract accepted. (Oral & Selected Poster at Sci-Mix Interdivisional Poster Session)*

2. “Preparation of hierarchical structured carbon nanofiber electrodes”

Y. Saito, M. Meguro, M. Ashizawa, H. Matsumoto

The 2013 Tsinghua Univ.-Tokyo Tech.-Kunming U. of Sci. & Tech. Workshops on Nanomaterials, Kunming, China, November 14-17, 2013. **(Poster)**

#### Domestic

1. “Preparation of hierarchical structured carbon nanofibers by electrospinning and electrodeposition”

H. Matsumoto, Y. Saito, M. Meguro, M. Ashizawa

51th Symposium on Polymer and Water, Society of Polymer Science, Japan, Tokyo, December 7, 2013. **(Oral)**

2. “Enhancement of electrical and mechanical properties of electrospun composite nanofiber yarns containing oriented graphene nanoribbons”

H. Matsumoto, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka,

2013 The Society of Fiber Science and Technology, Japan Autumn Meeting, Nagoya, Japan, September 5-6, 2013. **(Oral)**

3. “Enhancement of electrical and mechanical properties of electrospun composite nanofiber yarns containing oriented graphene nanoribbons”

H. Matsumoto, S. Imaizumi, Y. Konosu, M. Ashizawa, M. Minagawa, A. Tanioka,

The 4th Annual Meeting of the Nanofiber Society, Tsukuba, July 5, 2013. **(Poster)**

4. “Preparation of hierarchical structured carbon nanofibers by electrospinning and electrodeposition”

H. Matsumoto, M. Meguro, S. Imaizumi, M. Ashizawa, A. Tanioka,

The 4th Annual Meeting of the Nanofiber Society, Tsukuba, July 5, 2013 **(Poster)**.

5. “Preparation of hierarchical structured carbon nanofiber electrodes”

H. Matsumoto, M. Meguro, S. Imaizumi, M. Ashizawa, A. Tanioka,

2013 The Society of Fiber Science and Technology, Japan Annual Meeting, Tokyo June 12-14, 2013. **(Oral)**

6. “Preparation of hierarchical structured carbon nanofiber electrodes”

M. Meguro, S. Imaizumi, M. Ashizawa, H. Matsumoto, A. Tanioka,

62nd Society of Polymer Science, Japan Annual Meeting, Kyoto, May 29-31, 2013. **(Poster)**